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(54) Title: PROCESS FOR COATING A SUBSTRATE WITH A POWDER PAINT COMPOSITION

(57) Abstract

The invention relates to a process for coating a substrate with a powder paint composition. The powder paint particles are first charged by friction or induction in the presence of magnetic or non-magnetic particles, are next transported and are then applied to the substrate or applied to a transfer medium and subsequently transferred to the substrate, by means of an electric field between the substrate respectively the transfer medium and the means of transport whereafter the powder paint composition is cured or fused to obtain a powder coating.

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PROCESS FOR COATING A SUBSTRATE WITH A POWDER PAINT COMPOSITION

The invention relates to a process for coating a substrate with a powder paint composition.

In the powder paint industry, powder paints are usually electrically charged by means of a corona discharge or tribocharging. Then the powder paint is electrostatically applied to the object to be coated. In general, the electrostatic spraying technique involves use of corona and/or tribo charging guns as described in, for example, Misev "Powder Coatings Chemistry and Technology", pages 324-344, John Wiley, 1991.

Powder paints are being considered for use in the coil coating industry. Coil coating is a special application method in which coiled metal strips are unwound and then passed through pretreating, coating, and drying equipment before finally being rewound. Coil coating allows for very efficient coating of large surface areas in a short time at high throughput. However, the inherent limitation in powder paint spray gun capacity imposes restrictions on the rate of application of powder paints to the coil and on the reliability of the coil coating process. Hence, there is a strong need in this industry for a high speed but yet reliable continuous process for the application of powder coatings.

This appears, for example, from "Coil Coatings Strategies in change" by G.C. Simmons Polymers Paint Colour Journal, July 28, 1993, page 373.

An object of the present invention is to provide an improved process for coating a powder paint on a substrate, at rapid rates (e.g. 100 metres of substrate/minute) while yielding a high quality coating.

The process must also offer the possibility to treat large surface areas simultaneously.

The invention is characterized in that powder paint particles are first charged by friction or induction in the presence of magnetic or non-magnetic particles, are next transported and then applied to the substrate, or applied to a transfer medium and subsequently transferred to the substrate, by means of an electric field between the substrate respectively the transfer medium and the means of transport, whereafter the powder paint composition is cured or fused into a powder coating. The powder coating adheres to the substrate.

If a transfer medium is used, the powder paint particles are first applied to the transfer medium by means of an electric field, transported to the substrate by the transfer medium and then applied to the substrate by, for example, electrical, electrostatic or mechanical forces. Thermal processes can also be used in this application step.

The present process allows powder paint particles to be applied to substrates at rates up to, for instance, 200 meters of substrate/minute with film thicknesses of the cured film of between for example, 3 and 200 μm. Moreover, this process satisfies the need to eliminate multiple spray guns in a coil coating process.

The process according to the invention results in a substantially (e.g. more than 90%) fully coated substrate. In contrast, in, for example, a printing process the coverage is, for example, only 10% of the substrate.

The charging of the powder paint particles by friction or induction, the transporting or conveying and the application to substrates can be effected using processes commonly known in photocopying technology or laser printer technology (which processes are elucidated in, for example, L.B. Schein, Electrography and

Development Physics, pages 32-244, Volume 14, Springer Series in Electrophysics 1988; the disclosure of which is incorporated herein by reference).

According to a preferred embodiment of the invention the powder paint particles are mixed with magnetic or non-magnetic carrier particles to obtain friction charging whereupon the mixture is transported and the powder paint particles are applied to the substrate by means of an electric field between the substrate and the means of transport.

The powder paint composition may comprise any one of the known binder systems such as, for example, described by Misev, "Powder Coatings, Chemistry and Technology" (John Wiley and Sons, 1991), pages 9-171, the disclosure of which is incorporated herein by reference.

The powder paint composition can be tribo-modified, as described in, for example, US-A-5124387, the complete disclosure of which is incorporated herein by reference.

The powder paint composition can, if desired, comprise usual additives such as fillers, pigments, antioxidants, stabilizers, flow agents, catalysts and triboadditives as described in, for instance, US-A-5342723. The powder paint composition can also, for example, comprise additives for flow control purposes or for charge control purposes as described, for instance, in US-A-4960666.

The powder paint compositions can, for example, be prepared and characterized as described in, for example, the aforementioned Misev on pages 224-283 which disclosure is incorporated herein by reference. The selection of grinding, classifying and sieving equipment is important for obtaining the desired particle size of the powder paint particles.

The binder system can be a thermosetting or a thermoplastic system. Preferably, the binder system for

the powder paint is a thermosetting binder system.

Various types of curing reactions can be employed in thermosetting powder coatings for instance as disclosed in the afore mentioned Misev and radical curing systems such as UV-curing systems and electron beam curing systems. In many cases the thermosetting powder paint compositions comprise a binder system consisting of a resin and a crosslinker. Suitable resins include, for example, polyester resins, acrylic resins and alkyd resins.

Examples of suitable binders are: saturated carboxylated polyester resin / triglycidylisocyanurate (TGIC), saturated carboxylated polyester resin / epoxy resin, saturated carboxylated polyester resin / crosslinker containing hydroxylamide group, saturated carboxylated polyester resin / aliphatic oxirane, saturated hydroxylated polyester resin / isocyanate, polyester resin / diglycidyl phtalate containing crosslinker, saturated hydroxylated polyester resin / hexamethoxy-methylmelamine (HMMM), saturated hydroxylated polyester/glycoluril(derivative), saturated hydroxylated polyester/benzoguanamine (derivative), saturated hydroxylated polyester resin / amino resin, saturated hydroxylated polyester resin / phenolic resin, epoxy resin / amino resin, epoxy resin / phenolic resin, epoxy resin / anhydride, epoxy resin (selfcrosslinking), phenolic resin (selfcrosslinking), epoxy ester resin / amino resin, amino resin / isocyanate, acrylamide resin (selfcrosslinking), acrylic resin / hydroxy-functional compound, unsaturated acrylic resin (selfcrosslinking), unsaturated acrylic resin / vinylether, unsaturated polyester resin / vinylether and saturated epoxidized acrylic resin / dodecanedicarboxylic acid.

Preferred binder systems include a carboxylated polyester as resin and TGIC, an epoxy resin, a hydroxylamide group containing crosslinker (for example

Primid™) or an aliphatic oxirane (as disclosed in EP-A-600546) as crosslinker. Other preferred binder systems include hydroxylated polyester resin with HMMM or an isocyanate group containing crosslinker, an epoxy resin with a phenolic resin crosslinker and an epoxy ester resin with an amino resin crosslinker.

Upon curing or fusing of a powder paint composition a powder coating is obtained.

The median particle size (by volume) of the powder paint particles $X_{50,3}$ (as defined according to the description and notation at pages 12-14 of Mechanische Verfahrenstechnik by Prof. Rumpf (Carl Hansen Verlag, 1975)) can be for example below about 200 µm, and preferably, is between about 5 and about 60 µm.

The selection of the particle size depends on for example the desired final coating thickness for a given application.

The particle size distribution can be as broad as it is in conventional powder paint technology.

Preferably, the particle size distribution is relatively narrow. More preferably, the ratio $X_{75,3}:X_{25,3} < 3$ (according to the definition in the aforementioned Rumpf), since the efficiency of the development step may vary with the particle size.

It is one of the advantages of the process according to the present invention, that it is possible to apply particles having median particle sizes between about 5-30 µm. It is very difficult to apply these particles with conventional spray guns.

Carrier particles can be either magnetic or non-magnetic. Preferably, the carrier particles are magnetic particles.

Suitable magnetic carrier particles have a core of, for example, iron, steel, nickel, magnetite, γ-Fe_2O_3, or certain ferrites such as for example CuZn, NiZn, MnZn and barium ferrites. These particles can be of various

shapes, for example, irregular or regular shape.

Generally, these carrier particles have a median particle size between 20 and 700 μm. Preferably, the carrier particle size distribution is narrow and more preferably the ratio $X_{75,3}:X_{25,3} < 2$.

Exemplary non-magnetic carrier particles include glass, non-magnetic metal, polymer and ceramic material.

Non-magnetic and magnetic carrier particles can have similar particle size.

Preferably the carrier core particles are coated or surface treated with diverse organic or inorganic materials to obtain, for example, desirable electrical, triboelectrical and/or mechanical properties. Inorganic materials are described in for example US-A-4925762 and US-A-5039587. Organic coating materials include, for example, polymers having fluor-, silicone-, acrylic-, styrene-acrylic, melamine- or urethane-group. Mixtures of these polymers can also be used. Preferably a fluor containing polymer is used as coating.

For coating the carrier particles, any suitable method to coat a thin or thick layer on a powder surface, such as, for example spray coating in a fluidized bed or dry coating in a rotary kiln, can be used.

The carrier coatings can comprise suitable fillers or additives to control for example, triboelectrical, electrical or mechanical properties of the carrier coating. For example conductive materials such as, for example, carbon black and metal powder or charge controlling material and flow improving materials can be used.

The carrier particles may be conductive (as described in for example US-A-4076857) or non-conductive.

For direct application without a transfer medium, on a metal substrate, the carrier particles should be preferably non-conductive and they should have a well-defined high resistivity of, for example, 10^9-10^{11} Ohm at

10V potential and a break-through voltage above 1,000V (measured with a c-meter supplied by Epping GmbH).

In case of use of a transfer medium the carrier particles can be conductive or non-conductive.

Preferably, carriers particles having high voltage break through are used so that high electric fields can be used between transport means and substrate or transfer media to achieve a thick powder layer.

A developer comprises powder paint particles and carrier particles. A development method is a way of developing and a development unit is a complete system comprising of, for example, a developer roller (transport medium), mixing screw(s), a supply device, blades, detectors and the like. Other examples are described in, for example, GB-A-2097701, US-A-4147127 and US-A-4131081.

In the present invention the development method can be either one-component or two-component. According to a preferred embodiment of the invention the two-component development method, in which the carrier particles are mixed with the powder paint particles, is used.

Preferably, a combination of powder paint particles having a $X_{50,3}$ below 80 μm and a $X_{95,3}$ below 120 μm and carrier particles having a $X_{50,3}$ below 180 μm and a $X_{95,3}$ below 200 μm is used.

More preferably, a combination of powder paint particles having a $X_{50,3}$ below 30 μm and above 5 μm and a $X_{95,3}$ below 50 μm and carrier particles having a $X_{50,3}$ below 180 μm and above 5 μm and a $X_{95,3}$ below 200 μm is used.

In the two-component developer the amount of powder paint particles can be, for example, between about 1 and about 50 wt.% and preferably between about 5 and about 25 wt.% (relative to the amount of developer). It is an advantage of the process according to the invention that it is possible to use powder paint concentrations well in excess of 10 wt.%. Consequently, the amount of carrier particles can be between about 50 and about 99% by

weight (relative to the amount of developer) and preferably is between about 75 wt.% and about 95 wt.%.

The powder paint concentration can be externally or internally (in the development unit) controlled. External control can be effected by measurement of layer thickness of uncured or cured powder by, for example, optical, photothermical or dielectrical means. Internal control can be carried out in the developer station by means of powder paint concentration control by any suitable means like inductive control (see, for example, US-A-4147127 and US-A-4131081) or volume control.

In a two-component development method the powder paint particles are triboelectrically charged by intensive mixing and friction with the carrier particles.

In the process according to the present invention it is also possible to use a one component development method with the carrier particles being incorporated in the powder paint particles as disclosed in, for example, US-A-4803143 and US-A-4543312.

In a one-component development method the particles are charged by induction or friction, depending on the selection of the powder paint particles.

Both one- and two-component developers can be transported by magnetic, electric and/or mechanical transport.

Preferably, the means of transport is a conveying method.

The mixture is preferably conveyed by means of a magnetic roller as described in for example US-A-4460266. In addition to a magnetic brush apparatus also useful in the present process are, for example, non-magnetic cascade development (see page 94 of the hereinbefore incorporated reference of L.B. Schein), magnetic cascade development (as described in for example "The 9th International Congress on Advances in Non-Impact Printing Technologies/Japan Hardcopy '93, pages 133-140). In

addition also transport by air, for example, powder cloud development can be used. An exemplary process is described in for example US-A-2725304. Also jumping (projection) development (see for example Electrophotography, Fourth International Conference, pages 207-228, Nov. 16-18, 1981) can be carried out.

When two-component developers are used, the parameters which are relevant for the process (such as, for example, powder paint concentration, development potential and machine parameters) can be chosen depending on the application. This may lead to batch developer replacement, e.g. after certain time intervals or if certain parameters are out of a control range. Preferably, continuous developer material replenishment, as described in, for example, US-A-4614165, can be used to avoid process interruption for batch replenishment.

Suitable substrates to be coated include, for instance, metal (such as for example aluminium, steel, electrogalvanised steel and hot dip galvanized steel), textile, plastic and wood. Preferably, the process according to the invention is effected with use of coil-coating substrates. The preferred substrate is metal.

The substrate can have any desired shape such as band or sheet, i.e. continuous or discontinuous.

The substrate may be magnetic or non-magnetic. If a magnetic substrate and a magnetic developer are used, generally an intermediate transfer medium like a belt or a roller has to be placed between the magnetic roller and the substrate as for example disclosed in EP-A-354530.

If a transfer medium is used between the transport means and the substrate any suitable transfer medium like metallic drums, dielectric drums, foil from metals or polymers like silicone rubber belts, as described in "Proceeding of IS&T's Seventh International Congress on Advances in Non Impact Printing Technologies",

Vol. II, page 453-462, or composite materials can be used.

The process according to the present invention is preferably used in a coil-coating process or in a sheet-coating process. The coated substrates obtained with this sheet coating process can advantageously be used in the production of cans. Surprisingly, it was found that fully closed layers having a thickness of about 5 μm can easily be obtained with the process according to the invention whereas it is very difficult to obtain such layers with spraying techniques.

The process can also be used in a foil-coating process and furthermore in any process where a constant layer of powder paint has to be applied to a surface.

The pretreatment of substrates is important. Suitable pretreatment processes are discribed in, for example, "Pretreatment Processes and Materials" 1986 European Coil Coating Directory, pages 134-135.

The substrate can be pretreated or coated with for instance, a primer. Such a primer may be coated as a thin layer in wet form or by means of the process of the present invention.

Generally, more layers can be applied with or without intermediate fusing separately on the substrate or separately on the transfer medium and jointly transferred to the substrate.

A preferred process according to the present invention thus comprises charging of the powder paint particles by intensive mixing and friction with magnetic carrier particles, transport of carrier particles and powder paint particles with the aid of a magnetic roller and subsequent application of the powder paint particles to a substrate by means of an electric field between the substrate and the magnetic roller, whereafter the powder paint composition is made to cure or to fuse to a powder coating using techniques known in the art.

In this preferred process it is also possible to

apply a transfer medium as described previously.

The carrier particles may be dosed to a mixing arrangement in which, one or more means of intensive mixing such as, for example, worm wheels are present along with a magnetic roller. Suitable mixing arrangements are described in, for example, "Proceeding of IS&T's Seventh International Congress on "Advances in Non Impact Printing Technologies", Vol. 1, pages 259-265, the complete disclosure of which is herein incorporated by reference.

Next, an amount of powder paint particles is fed into the mixing arrangement which is selected so as to obtain a powder paint particles concentration of, for example, about 5-15 wt.% powder paint relative to the amount of carrier particles. In this way, a developer is formed.

During the intensive mixing and friction in the mixing arrangement, due to the action of the worm weels, the carrier particles and the powder paint particles become oppositely (tribo) electrically charged. A layer of electrically charged powder paint particles covers the carrier particles. The carrier particles subsequently act as carrier for the charged powder paint particles. Next, the developer is fed to the magnetic roller, on which a brush-like structure, also known as the magnetic brush, is formed. The magnetic roller transports the brush to the contact area with the substrate or transfer medium. In this way, powder paint particles, as well as carrier particles, become available at the contact area with the substrate or transfer medium. By applying a sufficiently strong electric field between the magnetic roller and the substrate or transfer medium the powder paint particles can be drawn from the brush to the substrate or transfer medium, onto which they adhere electrostatically. In the case a transfer medium is used, the powder paint particles are subsequently transported to the contact area of the transfer medium and the substrate and next transferred to

the substrate via one of the aforementioned transfer processes.

Finally, the magnetic brush is scraped off the magnetic roller as it is returned into the mixing bin.

As a result, a layer of powder paint particles forms on the substrate, which layer is substantially free from carrier particles, and can then be cured. Eventually an apparatus which can catch carrier particles can be introduced such as for example a catching equipment for residual carrier, as described in "Proceeding of IS&T Eighth International Congress on Advances in Non Impact Printing Technologies", pages 391-393. The thickness of said layer of powder paint particles can, for example, be controlled via the electric field strength between the magnetic roller and the substrate, the magnitude of the charge on the powder paint particles (e.g. by varying the concentration and the mixing time) and the roller speed.

The invention will be further described based on the following non-limiting examples.

<u>Examples</u>

<u>Example I</u>
<u>Production of a powder paint composition</u>

A powder paint was prepared by premixing 558 parts of saturated carboxylated polyester resin, (Uralac P5010™, supplied by DSM Resins), 42 parts by weight of triglycidylisocyanurate (TGIC; Araldite PT 810™, supplied by Ciba Geigy Ltd.), 300 parts by weight of titanium dioxide, (Kronos 2160™, supplied by Kronos Titan GmbH), 9 parts by weight of flow control agent (Resiflow PV5™, supplied by Worlée-Chemie GmbH) and 4.5 parts of benzoin in a "Diosna" V-30 batch mixer until the mixture is uniform and next melt kneaded in a Buss-Ko-Kneader PLK 46, (case setting temperature 120-130°C; kneading screw temperature 50°; 60 r.p.m.).

The cooled extrudate was milled first in a hammer mill to a particle size < 3 mm and then fed into a fluidized bed mill (Condux CFS8), having a nozzle diameter of 4 mm. The material was milled with 5 bar overpressure air pressure at 1900 r.p.m. of the classifier wheel incorporated in the mill obtaining a powder paint with a median particle size of 24 μm and a ratio $X_{75,3}/X_{25,3}$ ratio of 2.3.

Example II

Preparation of a carrier

998 parts by weight Cu-Zn-ferrite powder, having a median particle size of 81 μm and a ratio $X_{75,3}/X_{25,3}$ of 1,32 (both measured with the laser granulometer Cilas HR 850), were dry coated with 2 parts by weight polyvinylidenedifluoride (Kynar 301F™) by mixing both materials in a Lödige mixer and coating the polymer on the surface of the ferrite in a rotary kiln at 200°C under N_2-atmosphere to obtain a carrier with a medium size of 80 μm, a ratio $X_{75,3}/X_{25,3}$ of 1.32, a resistance of $1.1*10^{10}$ Ohm at a potential of 10V and a break-through voltage above 1,000V (both measured in a c-meter of Epping GmbH).

Example III

Preparation of a developer I

11% by weight of the powder paint composition according to Example I and 89% by weight of the carrier according to Example II were mixed at room temperature intensively in a "Skandex" paint shaker for 5 minutes to obtain a developer. The charge distribution of the developer was measured in a q-meter of Epping GmbH showing a sharp charge over diameter (q/d)-distribution with a median of 2.2 fC/10 μm, a standard deviation of 1.7 fC/10 μm and 5.2% oppositely charged particles.

Examples IV-VI

Preparation of developers II, III and IV

A coated ferrite carrier having a median particle size of 53 μm and a ratio $X_{75,3}/X_{25,3}$ of 1.47 (both measured with the laser granulometer Cilas HR 850), a resistance of $3.2*10^{10}$ Ohm at a potential of 10V and a break-through voltage over 1000V (both measured in a c-meter of Epping GmbH) was mixed with a powder paint composition according to Example I in a weight ratio carrier/powder paint 86/14, 80/20 and 75/25 to obtain the developers II, III and IV.

The charge distribution of the developers II and III was measured in a q/d-meter of Epping GmbH showing a sharp q/d distribution with a median of -7.5 and -5 fC/10 μm, a standard deviation of 2.6 and 1.7 fC/10 μm and 0.12 and 0.01 % oppositely charged particles, respectively.

Example VII

Coating on a substrate

The developer according to Example III was filled in a magnetic brush unit mounted in a distance of 2.5 mm of a rotating metal drum available as the ld-tester (developer life time tester) from Epping GmbH. On the rotating drum an aluminium sheet of 0.1 mm thickness was mounted. The rotation speed of the drum (i.e. coating speed) was 100 m/minute, the speed of the magnetic brush was 130 meter/minute in same direction as the drum. The doctor blade of the magnetic brush was adjusted to a distance of 1.5 mm to the magnetic roller. The magnetic pole was adjusted -10 degrees compared to the line between both rotating axes. The development potential of the drum against the developer roller was set to 1000V. The coated aluminium sheet, obtained after one development step, was then cured in an oven at 200°C to obtain a homogeneous powder coating with an average coating thickness of 25 μm and a tolerance of less than ± 10%.

Example VIII-XI

Coating on a substrate

Example VII was repeated and aluminium sheets were developed once or several times using the developers II-IV with the following results (in all cases the sheet was homogeneously coated):

TABLE I

developer	coating speed	no. of developments	thickness
II	60 m/min	3	18-22 μm
III	60 m/min	1	15-20 μm
IV	60/min	1	30-35 μm
IV	130 m/min	2	40-45 μm

Example XII

Preparation of a developer with low break-through voltage

A surface-oxidized, non-coated iron carrier of sponge shape having a median particle size of 154 μm and a ratio $X_{75,3}/X_{25,3}$ of 1.21. (both measured with the laser granulometer Cilas HR 850), a resistance of $1.3*10^{10}$ Ohm at a potential of 10V and a breakthrough voltage of 275V (both measured in the c-meter of Epping GmbH) was mixed with a powder paint composition according to Example I, where additionally the fine part of the particle size distribution was reduced by a further classifying step, in a ratio carrier/powder paint of about 97/3 to obtain developer V. It was not possible to increase the break-through voltage of the developer significantly by increasing the powder paint concentrations in the developer.

Example XIII

Dependence on coating speed and brush speed and angle of magnetic field

Example VII was repeated and aluminium sheets were developed once using developer V with the following results (in all cases the development voltage was -400 V).

TABLE II

coating speed	brush speed	angle of magnetic field	coating thickness
7.8 m/min.	45 m/min.	-15°	60-80 μm
15 m/min.	60 m/min.	-15°	30-60 μm
7.8 m/min.	45 m/min.	+ 5°	10-15 μm
7.8 m/min.	45 m/min.	-15°	30-40 μm

Example XIV

Preparation of a powder paint composition

A clear powder paint was produced analogous to Example I by using 300 parts by weight of a polyester resin (Uralac P5051™, supplied by DSM Resins), 300 parts by weight crosslinker (Araldite GB 7004™, supplied by Ciba Geigy), 3 parts by weight of flow control agent (Byk 361 supplied by Byk Chemie) and 2 parts of benzoin.

A powder paint was achieved with a median particle size of 10.8 μm and a ratio $X_{75,3}/X_{25,3}$ of 2.9.

Example XV

Preparation of a developer using a clear coat powder paint

Analogous to Example III a developer VI based on 155 parts by weight of the powder paint according to Example XIV and 845 parts by weight of carrier according to Example II was prepared.

Example XVI

Preparation of thin coatings

Analogous to example VII a sheet of aluminium was coated using developer VI (according to Example XIV) at a substrate speed of 30 m/min. and a brush speed of 78 m/min. with different development voltages. The results of the evaluation of the cured coating layers are listed below:

TABLE III

dev. voltage	average coating layer thickness	result of evaluation
-1000V	7.5 μm	high gloss, closed film
-800V	3.5 μm	high gloss, closed film

Example XVII

Heat transfer on a ferrous substrate

The developer according to Example XV was filled in a magnetic brush unit according to Example VII and then developed onto a rotating drum, which was coated with a 5 mm thick conductive coating of silicone rubber, filled with conductive carbon black. The coating speed of the drum was 30 m/min. and the speed of the magnetic brush 78 m/min. All other parameters were equal to those in example VII. The developed powder paint layer was then completely transferred to an iron foil of about 0.5 mm thickness, which was pressed to the rotating drum by a metal roller heated to 200°C and finally cured in an oven at 200°C to obtain a homogeneous powder coating film with an average coating thickness of 8 μm.

Example XVIII

Electrostatic transfer on a ferrous substrate

The developer according to Example XV was filled

in a magnetic brush unit according to Example VII. The rotating drum was coated with a 5 mm thick conductive coating of silicone rubber filled with conductive carbon black and an additional isolating silicone rubber layer of 0.3 mm thickness (being defined by a blade prior to drying). The coating speed of the drum was 30 m/min., the speed of the magnetic brush was 78 m/min. All other parameters were equal to Example VII. The powder coating layer was then transferred to an iron foil of about 0.5 mm thickness to a great extent, which was led to the rotating drum by a metal roller where a potential of -500V against the rotating drum was applied and finally cured in an oven at 200°C to obtain a homogeneous coated film with an average coating thickness of about 7 μm.

C L A I M S

1. A process for coating a substrate with a powder paint composition, characterized in that powder paint particles are first charged by friction or induction in the presence of magnetic or non-magnetic particles, are next transported and are then applied to the substrate or applied to a transfer medium, and subsequently transferred to the substrate, by means of an electric field between the substrate respectively the transfer medium and the means of transport, whereafter the powder paint composition is cured or fused to a powder coating.
2. A process according to Claims 1, characterized in that the substrate is metal, textile, plastic or wood.
3. A process according to any one of claims 1-2, characterized in that the substrate is metal.
4. A process according to any one Claims 1-3, characterized in that the powder paint particles are mixed with magnetic or non-magnetic carrier particles to obtain friction charging whereupon the mixture is transported and the powder paint particles are applied to the substrate by means of an electric field between the substrate and the means of transport.
5. A process according to any one of Claims 1-4, characterized in that the powder paint particles have a $X_{50,3}$ below 80 μm and a $X_{95,3}$ below 120 μm.
6. A process according to any one of Claims 1-5, characterized in that the powder paint particles have a $X_{50,3}$ below 30 μm and above 5 μm and a $X_{95,3}$ below 50 μm.
7. A process according to any one of claims 1-6, characterized in that the powder paint particle have a ratio $X_{75,3}:X_{25,3} < 3$.

8. A process according to any one of Claims 1-7, characterized in that the carrier particles have a $X_{50,3}$ below 180 μm and above 5 μm and a $X_{95,3}$ below 200 μm.

9. A process according to any one of claims 1-8, characterized in that the carrier particle have a ratio $X_{75,3}:X_{25,3} < 2$.

10. A process according to any one of Claims 1-9, characterized in that the powder paint composition comprises a thermosetting binder system.

11. A process according to Claim 10, characterized in that the binder system comprises of a carboxylated polyester resin and triglycidylisocyanurate, an epoxy resin, a hydroxylamide group containing crosslinker or an aliphatic oxirane as crosslinker, a hydroxylated polyester resin and hexamethoxymethylmelamine or an isocyanate group containing crosslinker, an epoxy resin with a phenolic resin crosslinker or an epoxy ester resin with an amino resin crosslinker.

12. A process according to any one of Claims 1-11, characterized in that the magnetic or non-magnetic carrier particles are selected from magnetic carrier particles consisting of a core of iron, steel, nickel, magnetite, γ-Fe_2O_3 or ferrites and non-magnetic carrier particles including glass, non-magnetic metal, polymer and ceramic material.

13. A process according to Claim 12, characterized in that the carrier particles are coated or surface treated.

14. A process according to any one of Claims 1-13, characterized in that the process comprises charging of the powder paint particles by intensive mixing and friction with magnetic carrier particles, transport of carrier particles and powder paint particles with the aid of a magnetic roller and subsequent

application of the powder paint particles to a substrate or to a transfer medium by means of an electric field between the substrate and the magnetic roller, whereafter the powder paint composition is cured or fused to a powder coating.

15. A two component developer comprising 1-50 % by weight powder paint composition according to any one of claims 10-11 relative to the developer.

16. A developer according to claim 15 comprising carrier particles according to any one of Claims 12-13 and powder paint particles.

17. A two component developer according to any one of Claims 15-16, characterized in that the powder paint particles have a $X_{50,3}$ below 80 μm and a $X_{95,3}$ below 120 μm and the carrier particles have a $X_{50,3}$ below 180 μm and a $X_{95,3}$ below 200 μm.

18. Use of powder paint particles having a $X_{50,3}$ below 80 μm and $X_{95,3}$ below 120 μm in a process according to any one of Claims 1-14 or in a developer according to any one of Claims 15-17.

19. Use of a thermosetting binder system in a process according to any one of Claims 1-14 or in a developer according to any one of Claims 15-17.

20. Use of carrier particles having a $X_{50,3}$ below 180 μm and a $X_{95,3}$ below 200 μm in a process according to any one of Claims 1-14 or in a developer according to any one of Claims 15-17.

21. Use of magnetic carrier particles consisting of a core of iron, steel, nickel, magnetite, γ-Fe_2O_3 or ferrites and non-magnetic carrier particles including glass, non-magnetic metal, polymer and ceramic material in a process according to any one of Claims 1-14 or in a developer according to any one of Claims 15-17.

22. Coated substrate wherein the coating is obtained from a process according to any one of Claims 1-14.

23. Use of a process according to any one of claims 1-14 in a coil-coating process or in a sheet-coating process.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 95/00390

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D5/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 72-40800T[25] & JP,B,47 021 712 (KANZAKI SEISHI KK) see abstract ---	1,5,6, 12,18, 21,22
A	EP,A,0 476 647 (HOECHST AG) 25 March 1992 see claims 1,11,12 see page 16, line 24 - line 45 Anwendugsbeispiele see examples 5,6 ---	1
A	EP,A,0 260 638 (HODOGAYA CHEMICAL CO. LTD.) 23 March 1988 see claim 1 see page 3, line 32 - line 42 --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

4

Date of the actual completion of the international search	Date of mailing of the international search report
24 January 1996	19. 02. 96

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Inte   onal Application No
PC I/NL 95/00390

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 516 (C-656) 17 November 1989 & JP,A,01 210 472 (MITSUI ENG & SHIPBUILD CO. LTD. ET AL) 24 August 1989 see abstract	1
A	GB,A,2 097 701 (SIEMENS AG) 10 November 1982 cited in the application see claim 1	1
A	US,A,4 147 127 (TERASHIMA I.) 3 April 1979 cited in the application see claim 1	1
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4

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PCT/NL 95/00390

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